High-Resolution Multispectral Scanning for Mesoscopic Investigation of Discoloration of Traditional Japanese Pigments

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Abstract. This study describes a non-invasive analytical imaging scanning technique utilizing multispectral images to study discoloration and degradation of pigments used in traditional Japanese artworks. The images have high spatial resolution which can achieve mesoscopic resolution (typically 0.1mm-10mm). Since the images are being scanned line by line instead of being recorded frame by frame, this enables accurate color and spectral recording of the material response from visible and near infrared irradiation. The multispectral images were used to reconstruct color information and spectral reflectance. The mathematical model is based on the Moore-Penrose pseudoinverse. Using mesoscopically resolvable images, it is possible to measure the spectral reflectance of pigments ranging from µm-mm ROI unlike conventional spectrometers that requires big sampling area. The significance of mesoscopically-resolved analysis is demonstrated by investigating the discoloration and degradation of natural and artificial Japanese pigments. The pigments were heated in air at 300°C and sampled every 10 minutes. It was observed that the pigments discolored at seemingly random clusters. The reconstruction of the spectral reflectance at different sizes of ROI reveals strong correlation with background reflection. The size of the initial discoloration sites makes it impossible to measure using conventional spectrometers. It was observed that by using submm ROI, it is possible to observe reflection and absorption patterns in the pigments which does not register with mm-scale ROI. The results have shown that mesoscopically resolvable multispectral images can be used effectively to study degradation and discoloration in pigments.

Keywords: Analytical imaging · Spectral reflectance · Mesoscopic · Multispectral · Japanese pigments

1 Introduction

Noninvasive and nondestructive analysis is important in the field of cultural heritage [1-3]. This is particularly significant since they are irreplaceable treasures which are in the making over centuries and even millennia. As a result, a lot of effort has been

given to the preservation, conservation and investigation of these objects. However, there is always conflict between conservators and investigators. On the one hand, conservators wants to preserve the integrity of the object by minimizing its exposure to damaging conditions such as prolonged exposure to uncontrolled humidity and temperature as well as unsafe ambient light. This meant that a lot of these precious artifacts are locked in a safe place never seeing the light of day. On the other hand, investigators could become overzealous in documenting and acquiring as much information as possible without so much regard on the integrity of the object. This is justified by saying that deteriorating even if it is kept in a controlled storage and not exposed to any harmful environment. Therefore this could warrant the argument for recording the state of the object before it is completely destroyed. Both arguments have merits but in the end, these cultural treasures belong to the world; not to the museum that is keeping them or the researchers that study them. Therefore there is need for an accurate but safe technique for investigating cultural treasures.

The most common analytical technique used for investigating cultural heritage is either based on X-ray or infrared radiation [4-13]. Some of the common techniques in art analysis are synchrotron radiation X-ray fluorescence (XRF) [4-7], X-ray absorption fine structure (XAFS) [7], X-ray absorption near edge structure (XANES) [8], x-ray diffraction (XRD) [9-10], particle induced x-ray emission (PIXE) [11], neutron diffraction [10], laser induced breakdown spectroscopy (LIBS) [12], Fourier transform infrared spectroscopy (FTIR) [8], Raman spectroscopy [13] and many more others. Visible light radiation is also used but mostly for qualitative analysis and visualization. However, like other forms of electromagnetic radiation, the interaction of visible light with matter can be quantified. We refer to this as analytical imaging.

Analytical imaging refers to the technique which uses image processing, data mining and pattern recognition to extract useful and relevant information about different properties of a material. This is based on the fact that a material subjected to an incident electromagnetic radiation behaves in a predictable and quantifiable way. The characteristic material response depends on the energy and frequency of the radiation. In the past imaging only refers to the visible region but due to the developments in optical sensors, images can be formed with almost any electromagnetic spectrum. In this study, focus was given to the visible to near infrared range of the electromagnetic spectrum. This radiation spectrum provides useful information about pigment characteristics which are not readily observable in other spectrum [14]. The material response is quantified based on its spectral properties, colorimetric information and spatial features. It is believed that the most important aspect of an imaging system is the acquisition of the images. Especially, in art investigation, it is vital to have not only an accurate digital archive of the artwork but as well as being able to use it for analysis. Without an image that has reliable spectral, spatial and color information, it would remain to be usable only as a visual tool. Therefore there is a great need for the development and implementation of a nondestructive and noninvasive means of analytical imaging which is capable of acquiring uninterpolated high resolution images able to accommodate small- to large-sized objects. The images should have high color reproducibility, reliable spectral information and accurate spatial resolution. This is the reason why the analyses were performed multispectrally with mesoscopic resolutions.

The use of multispectral system for material analysis has been investigated in the past [15-18]; the advances in CMOS and CCD technologies have enabled the production of high quality images with good color reproduction; finally, spectrometer technologies are making strides in producing devices with high spectral resolutions. These three aspects are important in analytical imaging. Although these technologies have been around for quite some time, there are still limitations. As mentioned previously; color reproducibility, spectral accuracy and spatial resolution is important. With the previous multispectral imaging systems, they have high spectral accuracy but lack in good color reproduction and spatial resolution. The advanced imaging devices have high color fidelity but lacks readily usable spectral information. Conventional spectrometers could only produce accurate spectral data. In addition, there is a limitation in the spot size or the region of interest (ROI). Normally, the ROI is in the range of few millimeters to centimeters. This could affect the accuracy of the spectral data when analyzing sub-millimeter spots. This is why a system capable of extracting color and spectral information with mesoscopic resolution is important. Mesoscopic (~0.1mm-10mm) dimension refers to the resolution between macroscopic (>1cm) and microscopic (<100µm) scale.

Mesoscopic imaging has been widely used biology but is still considered in its infancy compared to microscopic and macroscopic techniques [19]. In cultural heritage investigation, it is almost unheard of. However, there are parallels that can be drawn between biological imaging and cultural heritage imaging. In biological imaging, there are living organisms that remain largely inaccessible by current optical imaging methods due to the limitation on depth resolution that can be achieved beyond several microns [20]. Similarly, pigment analysis in cultural heritage requires sub-mm resolution since discoloration and degradation occur on random spots. Without the capability of resolving the images mesoscopically, it is very easy to miss important information. To address this concern, an analytical imaging technique using mesoscopically-resolved images was used to analyze pigment discoloration and degradation patterns on selected Japanese mineral pigments.

The pigments were artificially degraded by heating at high temperatures (~300°C) and observed at short time lapses to investigate the structural, colorimetric and spectral changes *in situ* and noninvasively. The influence of the ROI size on the spectral measurement was discussed as well as its dependence on background reflection. Based on the results, there is a strong argument that high resolution multispectral imaging could be a very useful tool for cultural heritage investigations.

2 Methods and Experiments

2.1 Multispectral Imaging and Spectral Reflectance Reconstruction

The multispectral images were captured with a monochromatic CMOS line-camera using spectral-cutting and band-pass filters. A total of eight images were taken which contain spectral information from 380-850 nm. The images were used to reconstruct spectral data cubes with a 5-nm resolution. The spectral data were then used to reconstruct spectral reflectance and colorimetric information. Referring to the physical model shown in Fig. 1, it may be inferred that the sensor response of an imaging device when an object is irradiated with visible and near infrared radiation is proportional to its

spectral reflectance. The sensor response, characterized by the image pixels, can be mathematically expressed as a function of the object's spectral reflectance, camera sensitivity, light source spectral radiance and system error. This is shown in Eq.1:

$$\mathbf{p} = \int \mathbf{C}(\lambda) L(\lambda) r(\lambda) d\lambda + \mathbf{e}$$
(1)

p is an M \times 1 sensor response vector from the M channel sensor, $C(\lambda)$ is an M \times 1 vector of spectral sensitivity of the sensor, $L(\lambda)$ is the spectral radiance of the illumination, $r(\lambda)$ is the spectral reflectance of the object, and **e** is an M \times 1 additive noise vector. For mathematical convenience, Eq.1 can also be expressed in vector form as follows:

$$\mathbf{p} = \mathbf{C}\mathbf{L}\mathbf{r} + \mathbf{e} \tag{2}$$

where **C** is an $M \times N$ matrix of spectral sensitivity of the sensor, **L** is an $N \times N$ diagonal matrix of spectral radiance of the light source, and **r** is an $N \times 1$ spectral reflectance vector of the target. In this study, an indirect method of solving the vector relationship between the sensor response and spectral reflectance is implemented. The technique is based on Moore-Penrose pseudoinverse. The vector relationship is solved without the prior knowledge of the spectral characteristics of the system by using a learning sample. The learning sample can be used to estimate a conversion matrix to approximate the camera and light source spectral characteristics without having to worry about systemic changes. This makes the method device independent.

Since the samples characterized in this study are Japanese pigments, a specially designed and selected palette of Japanese organic and inorganic mineral pigments was used as the learning sample. The learning sample is composed of 173 pigments. They represent a wide variety of pigments including natural and artificial; organic and inorganic; ancient and modern; and a broad spectrum of colors with distinct spectral sensitivities at the infrared region. These learning samples are used to estimate the spectral reflectance. Going back to Eq. 2, it can be rewritten as,

$$\mathbf{p} = H\mathbf{r} \tag{3}$$

where *H* represents the camera and light source spectral characteristics and **e** is omitted for simplicity. *H* in this case represents an M x N matrix with M being the number of spectral channels and N as the number of spectral interval covering the desired spectral range. The pseudoinverse model is a modification of the Wiener estimation by regression analysis [14]. In this model, a matrix *W* is derived by minimizing ||R - WP|| from a known spectral reflectance of a learning sample, *R*, and the corresponding pixel values, *P*, captured at a certain spectral band. The matrix *W* is given by Eq.4:

$$W = RP^{+} = RP^{t} (PP^{t})^{-1}$$

$$\tag{4}$$

Where P^+ represents the pseudoinverse matrix of *P*. By multiplying the derived matrix *W* to the pixel value of the target image, **p**, the spectral reflectance $\hat{\mathbf{r}}$ can be estimated using Eq.5:

$$\hat{\mathbf{r}} = W\mathbf{p}$$
 (5)

The size of the matrices used in Eq.4 and Eq.5 is a function of the number of learning sample k, number of multispectral bands M and number of spectral reflectances N. In this study, the value of M and N depends on the spectral range and number of filters used. The number of filters used is M=8 while N is either 95 for the 5-nm interval spectral reconstruction between 380-850 nm. The images were taken at 600 dpi (~42 µm/pixel). Since the images have high spatial and spectral resolution, the ROI for spectral reflectance reconstruction is reliable up to pixel level. This enables spectral measurement at spatial resolutions which are not possible with conventional spectrometers. The effect of the ROI size is investigated by reconstructing the spectral reflectance for the discolored Japanese pigments.

2.2 Pigment Discoloration and Characterization

In this study, a method for investigating pigment discoloration and degradation mesoscopically is described. This was achieved by taking an accurate recording of discoloration as it happens *in situ* using high resolution multispectral imaging and spectral reflectance reconstruction. There are two groups of pigments selected as test cases. All pigments are in powder form. The first group is composed of copper-based pigments such as malachite and azurite. The second group includes iron-based pigments specifically hematite and ochre. Whenever possible, both natural and artificial pigments were used. All but ochre has an artificial pigment corresponding to the natural pigment. A total of seven pigments were subjected to extreme temperature.

The pigments were heated at 300°C in air for 36 hours. Sampling was done for the first hour of heating every 10 minutes. At this interval, the pigments were taken out of the heating chamber, scanned multispectrally then returned to the chamber for additional heating. Extra care was observed when taking the pigments in and out of the chamber to minimize the disturbance. This was done to preserve the initial discoloration sites which occur at random. After one hour, the sampling was halted until the pigments underwent a 36-hour heating at extreme temperature. At this point, the pigments would have had enough time to decompose completely. The recorded multispectral images where then used for spectral reflectance measurement with pin-point accuracy.

The analytical imaging results provides a lot of useful information on the degradation mechanism of the pigments. Through the analysis performed in this study, it was possible to observe degradation and discoloration associated with structural changes, reflectance and absorbance patterns.

3 Results and Discussion

Spectral reflectance is the plot of the reflectance of a material as a function of wavelength. In optics and photometry, reflectance is the fraction of the incident radiation that is reflected by a surface. It is a directional property of materials. Similar to other properties which can be characterized by advanced analytical techniques (e.g. X-ray analysis), the response from visible light and near infrared irradiation is characteristic of the material and can provide useful insight on its properties. In this study, spectral reflectance measurements were performed on discolored and degraded Japanese pigments by analytical imaging. This was achieved by acquiring high-resolution multispectral images of the pigments using a flat-bed scanner. The method of reconstructing spectral and colorimetric information is described in the pervious section. The scanning resolution was 42μ m/pixel. Since the images were taken at high resolution it has good spatial resolution. This enables spectral reflectance measurement at mesoscopic levels. What is significant about this is that conventional spectrometers require a big sampling area, normally about few millimeters. This ROI is acceptable for investigating bulk samples with homogeneous spectral distribution but this is not usually the case. Some of these spectrometers may also require contact with the sample to minimize ambient light interference. This can become problematic when investigating cultural heritage which requires non-invasive analysis.

ROI is not only an issue connected to the sampling area but it is also related to the amount of reflection from the background. For thick and homogenous sample this is not a problem since the re-reflection is less likely but for thin samples this is a serious concern. The background reflection is proportional to the size of the ROI. Since the usual method takes the average of big sampling area, a lot of background re-reflection is also recorded. This is demonstrated by Fig. 1. In this figure, the spectral reflectance of the pigment were measured for eight different square ROI with 1pxl, 2pxls, 4pxls, 8pxls, 16pxls, 32pxls, 64pxls and 128pxls corresponding to dimensions depicted in the figure. It can be seen from the figure that the reflectance is not homogeneous where white spots on the images corresponding to specular reflection are visible. The figure shows the strong correlation of background reflection to ROI.

The strong background reflection from big ROI spectral reflectance measurement is acceptable in some cases as long as this is carefully observed. Since measurements are usually done using a fixed ROI, it is possible to subtract the background effectively. However the issue with big ROI is not only because of this but mainly because of its limitation in size. Big ROI is not a problem if the area of interest is bigger than the sampling area. However, there are cases that it is the other way around. For example, in the discoloration and degradation experiment performed in this study, it was observed that pigment discoloration initiates at seemingly random spots. Although in theory these events are not really random. This initiation at certain spots may be analogous to how mechanical defect, like cracks propagate. Cracks are initiated and propagate from regions of high stress concentration. Similarly, the pigment's initial discoloration spots are region with high chemical reaction sites. These sites require less time and push for chemical reaction to begin. Since the pigments were being heated at a fast rate, the pigment particles will degrade at different rates. This phenomenon is depicted by Fig.2. This behavior may also be attributed to the form of the pigments used as samples. The pigments were prepared as powders. Since there was no binding media holding the particles together, the surface to volume ratio is magnified significantly at the micron or submicron level as compared to bulk samples [21]. This then raises a question whether studying the discoloration and degradation in powder form is a good idea since pigments are applied with a binding media when





Fig. 1. Pictogram of the sampling area for measurement with the corresponding spectral reflectance. The graph shows the effect of ROI to the background re-reflection.



Fig. 2. Schematic diagram depicting how pigments degrade and discolor. The sites seem to appear at random but are actually associated to the surface energies of the pigments.

used in cultural heritage pieces. Although this is true, the mechanism for pigment degradation would still be the same. It will begin at favorable spots and not happen instantaneously through out the entire object. The binding media would affect the rate of degradation since it holds agglomerates of powder which could behave as bulk samples instead of particles. The discoloration and degradation of painted pigments were reported elsewhere [3]. In this study, the focus was given to how discoloration sites are initiated and the scale at which it happens.

The size of the initial discoloration site is in order of sub-mm to few millimeters. Measurement of the spectral reflectance can be a problem. This is where a mesoscopic spectral reflectance measurement is advantageous. Since these sites are very small, they are very easy to miss and not very visible with the naked eye. The problem with conventional spectral measurement is that it normally does not have a high-resolution display of where the measurements are being taken. This entails that the measurements were taken as-detected or by blind-sampling. Using the high-resolution recording of the pigments sample, it is very easy to pan through the entire surface and zoom in to specific area with great details. As a test case, Fig.3 shows the discoloration of natural azurite taken at 10-minute interval. It was observed (circled in red) that discoloration site started to appear after 10minutes of exposure. After 20 minutes, more sites started to appear and continued to appear until the pigments were completely transformed after 36 hours of heating. A similar observation was seen for natural malachite pigments. However, in the case of artificial azurite and malachite pigments, there were no visible signs of degradation. This would be discussed in detail in the succeeding section.



Fig. 3. Discoloration and degradation pattern of natural azurite pigments. It was observed that the discoloration sites seemed to appear sporadically.

Fig.4 shows another type of spectral measurements. In this case, three spots were selected the spots were measured using two different ROI size. The first one is 42µm and the other one is 2.7mm. P1 and P3 are points with visible discoloration while the color in P2 remained unchanged after 20 minutes. The size of the discoloration sites at P1 and P3 is about 1mm. Since the second ROI is bigger than the desired sampling area, the measurement includes area which are does not exhibit visible discoloration yet. The effect of ROI to the accuracy of the measurement is shown in Fig.5. Using the small ROI it was possible to distinguish between discolored and not discolored pigments. Unfortunately, this is still a physical limitation of normal spectrometers. However this highlights the advantage of using analytical imaging. With this method, it is not only possible to measure mesoscopically but the measurements need not be taken blindly. The accuracy of the spectral reflectance reconstruction is reported elsewhere [22].



Fig. 4. Spectral reflectance measurement at different spots on the pigment after 20 minutes of exposure to high temperature



Fig. 5. Spectral reflectance at three different points measured at two ROI. It was not possible to distinguish the spectral reflectance of discolored pigments using the big ROI.

Finally, Fig.6 shows another advantage of using small ROI for spectral reflectance measurement. The figure shows the spectral reflectance of heated artificial azurite. Visually, there was no distinguishable change in color but the spectral measurement at

42µm reveals otherwise (Fig.8a). This suggests that it is not often reliable to depend on visual signs as indicator for degradation since the human vision is sensitive to a limited spectrum of visible radiation. Fig.8b seems to support this observation as characterized by overlapping spectral reflectance. These measurements were performed at big ROI (~2.7mm). However, XAFS and XANES measurements agree with the pattern observed at small ROI measurements. More discussion is reserved for the next section. In addition, as pointed out previously, high background reflection is observed with big ROI.



Fig. 6. Spectral reflectance measurement of degraded artificial azurite at (a) $42\mu m$ ROI and (b) 2.7mm ROI

4 Conclusion

This study presented a method for investigating the discoloration and degradation mechanism of traditional Japanese paintings. The technique is based on analytical imaging through spectral reflectance reconstruction from multispectral images. The data processing technique used a mathematical model based on the Moore-Penrose pseudoinverse. The images were taken at high resolutions (~42µm/pixel) which means that it has high spatial resolution, good color reproduction and accurate spectral reconstruction. The spectral measurements could be done remotely and noninvasively which satisfies an important requirement of cultural heritage investigation. Due to the high spatial resolution of the images, the spectral measurements can be done at mesoscopic scale. This proved to be useful in understanding the discoloration and degradation patterns of selected Japanese mineral pigments. The technique provided great flexibility in the ROI size which is not usually available with conventional spectrometers. The results have shown that the ROI size is highly correlated with the background reflection which is important in detecting small changes in spectral reflectance. In addition, it is crucial that the ROI of the measurement is smaller than the size of the object. In the case of the initiation site of pigment discoloration this usually is in the sub-mm or mesoscopic scale. Accurate spectral reflectance measurements were done using mesoscopic ROI from multispectral images. It was also possible to detect small changes in the spectra which are not observed from big ROI. Overall, the results have shown that high resolution multispectral scanning has great potential for the noninvasive investigation of cultural heritage.

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